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ABSTRACT

This document is an instructional module package prepared in objective form for use by an instructor familiar with hardness analysis using the EDTA method and the calculation of hardness given metal ion concentrations and a factor table. Included are objectives, an instructor guide, student handouts, and transparency masters. A video tape is also available from the author. This module considers principles of hardness, calculation of hardness, preparation of reagents for the EDTA method, calculation of results and interferences and inhibitors. (Author/RH)

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HARDNESS ANALYSIS

Training Module 5.215.2.77

Prepared for the

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September, 1977

SE 024 157

Module No:	Module Title: Hardness Analysis
	Submodule Title:
Approx. Time: 3.0 hours	Topic: Summary

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Determine the Hardness of water as mg/l $CaCO_3$ using the EDTA titrimetric method and the calculation method.
2. Describe hardness as a property of water.
3. List 3 methods of inhibiting the interference of certain metal ions.

Instructional Aids:

Softening videotape
Transparencies Hd1-Hd4

Instructional Approach:

Lecture, discussion, videotape viewing, lab practice

References:

1. "Standard Methods for the Examination of Water and Wastewater" 14th edition.
2. G.V.James, "Water Treatment" 3rd ed., London: Technical Press, 1965, pp. 107-138.

Class Assignments:

Module No:	Module Title: Hardness Analysis
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Description of hardness

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Describe at least two sources of hardness in water.
2. Describe two negative effects of hard water.
3. Explain the difference between carbonate hardness, non-carbonate hardness and total hardness.

Instructional Aids:

Instructional Approach:

Lecture/discussion

References:

Standard Methods, pp. 200-201.

Class Assignments:

None

Module No: Hd	Topic: Description of hardness
Instructor Notes:	Instructor Outline:

1. Hardness is caused by poly valent metal ions which precipitate soap primarily Ca^{2+} and Mg^{2+} but also Al^{3+}, Zn^{2+}, Fe^{2+}, etc.

2. Negative effects:
   a. Precipitates soap "bath-tub" ring
   b. Causes scale to form on pipes and boilers

3. Types of hardness:
   a. If total hardness is greater than bicarbonate plus carbonate alkalinity, then:
      i. carbonate hardness equals alkalinity
      ii. non-carbonate hardness is total hardness minus carbonate hardness
   b. If total hardness is less than bicarbonate plus carbonate alkalinity then total hardness equals carbonate hardness and non-carbonate hardness is zero.

Module No:	Module Title: Hardness Analysis
	Submodule Title:
Approx. Time: 0.75 hours	Topic: Principles of Hardness Determination

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Calculate water hardness given a list of metal ion concentrations and a factor table.
2. Briefly explain the principles behind the EDTA method.
3. Describe the titration end point color change.

Instructional Aids:

1.Transparency Hdl-hardness factors

2.Softening videotape

Instructional Approach:

Lecture/discussion, videotape viewing

References:

Standard Methods pp. 200-208

Class Assignments:

None

Module No: Hd	Topic: Principles of Hardness Determination

Instructor Notes:	Instructor Outline:
Transparency Hd-1 hardness factors	1. Total hardness is equal to the sum of the ion concentrations time s the hardness factor. E.G.: A sample contains 108 mg/l Ca, 82 mg/l Mg, 20 mg/l Zn. Total Hardness 108X2.497=269.7 82X4.116=337.5 20X1.531=30.6 637.8 mg/l as $CaCO_3$
Softening Video tape	2. Show video tape, answer questions concerning titration. 3. Point out color change at end-point of titration.

Module No:	Module Title: Hardness Analysis
	Submodule Title:
Approx. Time: 0.25 hours	Topic: Safety

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Locate the following in the laboratory and demonstrate proper use: emergency shower, fire extinguisher, eye wash, first aid kit.
2. Select and use safety glasses, lab coat or apron and gloves in the appropriate situation.
3. Describe any hazards associated with hardness analysis.

Instructional Aids:

Hand-out of safety rules for the laboratory.

Instructional Approach:

Lecture/demonstration

References:

Basic laboratory skills module

Class Assignments:

Read lab safety rules.

Module No: Hd	Topic: Safety
Instructor Notes:	Instructor Outline:
	1. Point out and state purpose of each piece of safety equipment. 2. Safety glasses should be worn in the preparation of the buffer solution and in titration to prevent liquid from splashing in eyes. 3. No severe hazards, preparation of buffers involves NH_3 and HCl.

Module No:	Module Title: Hardness Analysis
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Preparation of reagents

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Properly prepare the following reagents: Buffer solution, standard titrant, standard calcium solution.
2. Properly prepare the indicator solution.
3. Explain how to prepare the sample, standard, or blank for titration.

Instructional Aids:

Transparency Hd2- required reagents

Instructional Approach:

laboratory practice

References:

Standard Methods pp. 203-205.

Class Assignments:

None

Module No: Hd	Topic: Preparation of Reagents

Instructor Notes:	Instructor Outline:
Transparency Hd-2 Required Reagents 1.a. 16.9 g NH_4Cl, 143 ml con NH_3, 1.25 g MgEDTA, dilute to 250 ml with H_2O 1.b. 3.723 g EDTA per liter 1.c. 1.0 g $CaCO_3$ in 500 ml flask. Add 6 M HCl until dissolved, 200 ml H_2O, boil, adjust pH with 3 N NH_3 dilute to 1 l. 2. 0.5 g Black T, $NH_2OH \cdot HCl$, 4.5 g in 100 ml ethanol(95%).	1. Solutions may be obtained already prepared commercially or students may prepare them in small groups a. buffer b. standard titrant c. standard calcium 2. Indicator solution:suggest solution form Eriochrome Black T. 3. Sample preparation: Add 2 ml buffer to 25 ml sample, 2 drops indicator,White light is important.

Module No:	Module Title: Hardness Analysis
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Titration of Standard and Water Samples

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Determine the concentration of a prepared $CaCO_3$ standard solution.
2. Titrate the $CaCO_3$ solution and calculate the concentration of EDTA titrant.
3. Titrate the sample solution.

Instructional Aids:

Transparency Hd3- Titration diagram

Instructional Approach:

Laboratory practice

References:

Standard Methods, p. 205.

Class Assignments:

None

Module No: Hd	Topic: Titration of Standard & Water Samples
Instructor Notes:	Instructor Outline:
	1. Concentration of $CaCO_3$ solution. In mg/ml = g $CaCO_3$ / volume in liters $M = \frac{gCaCO_3}{volume \times 100}$
Transparency Hd-3 Titration Diagram	2. Concentration of titrant M(EDTA)X ml EDTA $= M(CaCO_3) X ml(CaCO_3)$ $M(EDTA = \frac{M(CaCO_3) \times ml(CaCO_3)}{ml(EDTA)}$ $mg/ml(CaCO_3 \text{ equivalence}) = \frac{(mg/ml\ CaCO_3) X\ mlCaCO_3}{ml(EDTA)}$
	3. Titrations should be done in duplicate at least.

Module No:	Module Title: Hardness Analysis
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Calculation and Reporting Results

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Calculate hardness of a water sample from titration and standardization data.
2. Properly report hardness depending on how the number was determined.

Instructional Aids:

Instructional Approach:

Lecture/discussion

References:

Standard Methods, pp. 201-206.

Class Assignments:

None

Module No: Hd	Topic: Calculation and report of results

Instructor Notes:	Instructor Outline:

1. Calculation of hardness

   $$\text{Hardness} = \frac{(\text{ml EDTA})}{(\text{ml sample})} \times (\text{EDTA concentration})$$

   as $CaCO_3$ in moles per liter

   OR

   $$\text{Hardness} = \frac{(\text{ml EDTA})}{(\text{ml sample})} \times \frac{(\text{EDTA equivalence})}{1000}$$

2. Report:

   a. Hardness (EDTA)

   b. by Calculation:

      Hardness (Ca, Mg, Sr, etc.)

Module No:	Module Title: Hardness Analysis
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Interferences and Inhibitors

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Describe the purpose of inhibitors.
2. Describe the preparation of inhibitors.
3. List three interfering ions.

Instructional Aids:

Transparency Hd4- Inhibitor chart

Instructional Approach:

Lecture/discussion

References:

Standard Methods, pp. 202-204.

Class Assignments:

None

Module No: Hd	Topic: Interference and Inhibitors

Instructor Notes:	Instructor Outline:
Transparency Hd-4 Inhibitor chart	1. Inhibitors added: a. to provide sharp end point b. to prevent interference from other ions by complexing, reducing or precipitating them 2. Inhibitors: a. I NaCN b. II Na_2S c. III $NH_2OH \cdot HCl$ (part of indicator) 3. Interfering ions: Al, Ba, Cd, Co, Cu, Pb, Ni, Sr, Zn.

Exam Questions

Hardness Analysis
Description of hardness

1. Name two metal ions which contribute to water hardness.

2. Hardness in water is undesirable because it will react with soap to form _____.

3. If total hardness is less than the bicarbonate plus carbonate alkalinity, what will the non-carbonate hardness be equal to?

Principles of Hardness Determination

4. If a water sample contains 100 mg/l Ca^{2+}, 10 mg/l Mg^{2+}, what is the hardness as mg/l $CaCO_3$? Factors are Ca: 2.497, Mg: 4.116.

5. In the EDTA titration method, one EDTA molecule combines with _____ calcium ion(s).

6. In the EDTA titration of hardness in which the Eriochrome Black T indicator is used, the solution turns from _____ to _____ at end-point.

Safety

7. Which device in the laboratory is used to wash acid from eyes?

8. When a solution which contains ammonia is prepared, what safety device should be worn?

9. True or False: Ammonia has a strong odor.

Preparation of Reagents

10. What is the purpose of the buffer solution?

11. The name of the indicator used in the hardness determination is:
    a. phenolphthalein
    b. hydroxylamine
    c. methyl red
    d. Eriochrome Black T

12. Prior to titration buffer solution and _____ should be added to the water sample to be analyzed.

Titration of Standard and Water Sample

13. If 1.0 g of $CaCO_3$ is dissolved in 1.0 liters of solution, what is the concentration of that solution in mg/ml?

14. If it takes 25 ml of an EDTA solution to titrate 30 ml of a $CaCO_3$ solution which is 0.01 M concentration, what is the molarity(M) of the EDTA solution?

15. What type of light should be used to illuminate the sample during titration?

Calculation and Reporting Results

16. An EDTA solution was found to be equivalent to 0.95 mg $CaCO_3$ per ml. It took 20.0 ml of this solution to titrate 25.0 ml of a water sample. Calculate the hardness of the water sample in mg/l $CaCO_3$.

17. If the hardness in a water sample is reported as 600 mg/l as $CaCO_3$ hardness(EDTA), what method was used to determine this number?

Interferences and Inhibitors

18. True or False: One purpose of an inhibitor is to give a clear, sharp change of color at the end point.

19. Name a chemical used in one of the inhibitors.

20. Which of the following would be considered as interfering ion?
    a. cobalt
    b. magnesium
    c. calcium
    d. sodium

HARDNESS ANALYSIS

EQUIPMENT LIST

1. 250 ml volumetric flask
2. analytical balance
3. ammonium chloride
4. concentrated ammonia
5. magnesium ethylenediamine tetraacetate
6. distilled water
7. eriochrome black T
8. hydroxylamine hydrochloride
9. 50 ml beaker
10. 100 ml volumetric flask
11. 95% ethyl alcohol
12. disodium ethlenediamine tetraacetate dihydrate
13. 1 ℓ volumetric flask
14. 1000 ml graduated cylinder
15. 1 ℓ polyethylene bottle
16. calcium carbonate
17. 500 ml erlynmeyer flask
18. concentrated hydrochloric acid
19. bunsen burner
20. ringstand and ring
21. methyl red indicator solution
22. 2 - 50 ml burets
23. 25 ml pipet
24. 1 ml pipet
25. 5 - 125 ml erlynmeyer flasks
26. 5 - eyedroppers and bulbs

Laboratory Procedure

I. Preparation of Reagents and Standards
   A. Obtain all the equipment, supplies, and chemicals listed on the "equipment" handout.
   B. Prepare the following solutions:
      1. Buffer solution: To a 250 ml volumetric flask, add 16.9 g ammonium chloride (NH_4Cl) and 143 ml concentrated ammonia. Mix to dissolve. Add 1.25 g magnesium ethylenediamine tetraacetate (MgEDTA). Fill to the mark with distilled water, mix. If necessary refill to the mark with water mix. Label the flask.
      2. Indicator. Add 0.5 g eriochrome black T and 4.5 g hydroxylamine hydrochloride (NH_2OH-HCl) 50 ml beaker, mix well and transfer to a 100 ml volumetric flask. Add 95% ethanol to the mark. Mix to dissolve. Label the flask.
      3. EDTA titrant. Weigh 3.723 g disodium ethylenediametetra-acetate dihydrate ($Na_2\ H_2\ C_{10}\ H_{12}\ O_8\ N_2 - 2H_2O$ or Na_2EDTA) on an analytical balance and transfer to a 1 l volumetric flask. Add 500 ml distilled water, swirl to dissolve. Dillute to the mark with distilled water. Mix and transfer to a polyethlene bottle, label the bottle.
   C. Prepare the following standard solution: weigh 1.000 g anhydrous primary standard grade $CaCO_3$, calcium carbonate on an analytical balance and record the exact mass. Quantitatively transfer the $CaCO_3$ to a 500 ml erlynmeyer flask. Place a funnel on the neck of the flask and add 6 M hydrochloric acid (prepared by mixing equal parts concentrated HCl and distilled water) a little at a time until bubbling has ceased and all the $CaCO_3$ has dissolved. Add 200 ml distilled water and boil with a bunsen burner for five minutes. Cool.
   Add 2 drops methylred indicator. Mix. If the solution is yellow, add 6 M HCl dropwize until orange. If the solution is red add 3M NH_3 (ammonia) [prepare by dissolving 200 ml concentrated ammonia in distilled water to make a 1 liter solution] dropwize until orange. Transfer the solution to a 1 liter volumetric flask. Dilute to the mark with distilled water. The concentration of the solution in mg/ml $CaCO_3$ is numerically equal to the mass in grams $CaCO_3$ added.

II. Titration
   A. Titration of standard. Fill a 50 ml buret with EDTA solution. Fill another buret with standard Ca solution. Record the initial readings of each buret. Add 25 ml Ca solution to a 125 ml erlynmeyer flask. Add 25 ml distilled water. Add 1 ml buffer, add 2 drops indicator. Add EDTA titrant slowly with swirling in white light until the solution turns from red to blue (end-point). Record the final values of both burets. Repeat the titration twice, record results on data sheet. Volume of each solution used is equal to the difference between final and initial buret readings. The $CaCO_3$ equivalence of the EDTA is equal to the g $CaCO_3$ weighed times ml $CaCO_3$ solution used divided by ml EDTA solution. Average the three values. Call this value B.

Hardness Analysis

Data Sheet

Sample Number_____

Preparation of standard $CaCO_3$

	Mass of container plus $CaCO_3$	_____g
	Mass of container	_____g
(d)	Mass of $CaCO_3$	_____g
	Concentration $CaCO_3$ standard	_____mg/ml

Standardization of EDTA solution

		I	II	III
	Final Ca buret	_____ml	_____ml	_____ml
	Initial Ca buret	_____ml	_____ml	_____ml
(e)	ml Ca used	_____ml	_____ml	_____ml
	Final EDTA buret	_____ml	_____ml	_____ml
	Initial EDTA buret	_____ml	_____ml	_____ml
(f)	ml EDTA used	_____ml	_____ml	_____ml
(g)	EDTA equivalence = $\frac{dxe}{f}$	_____mg/ml	_____mg/ml	_____mg/ml

B=Average EDTA equivalence _____mg/ml $\frac{(I+II+III)}{3}$

Sample Titration:

	I	II	III
Final EDTA Buret	_____ml	_____ml	_____ml
Initial EDTA buret	_____ml	_____ml	_____ml
Volume EDTA Used	_____ml	_____ml	_____ml

A-Average EDTA volume $\frac{(I+II+III)}{3}$ _____ml

Hardness (EDTA)=$\frac{AxBx1000}{25}$ = _____mg/ℓ as $CaCO_3$

Comments:

Analyst_____ Date_____

TRANSPARENCY HDI

Hardness Factors

Metal ion	Factor
Ca	2.497
Mg	4.116
Sr	1.142
Fe	1.792
Al	5.564
Zn	1.531
Mn	1.822

TRANSPARENCY HD2

Required Reagents for Hardness Analysis

Buffer solution:

16.9g NH_4Cl, 143 ml con NH_3, 1.25g MgEDTA
Dilute to 250 ml with H_2O.

Standard titrant (0.01MEDTA)

3.323g $Na_2EDTA \cdot 2H_2O$. Dilute to 1000 ml.

Standard Calcium (0.01M$CaCO_3$)

1.000g$CaCO_3$ (anhydrous), 6M HCl until dissolved, 200ml H_2O. Boil to expel CO_2. Cool, add methyl red; adjust pH with NH_3. Dilute to 1000 ml

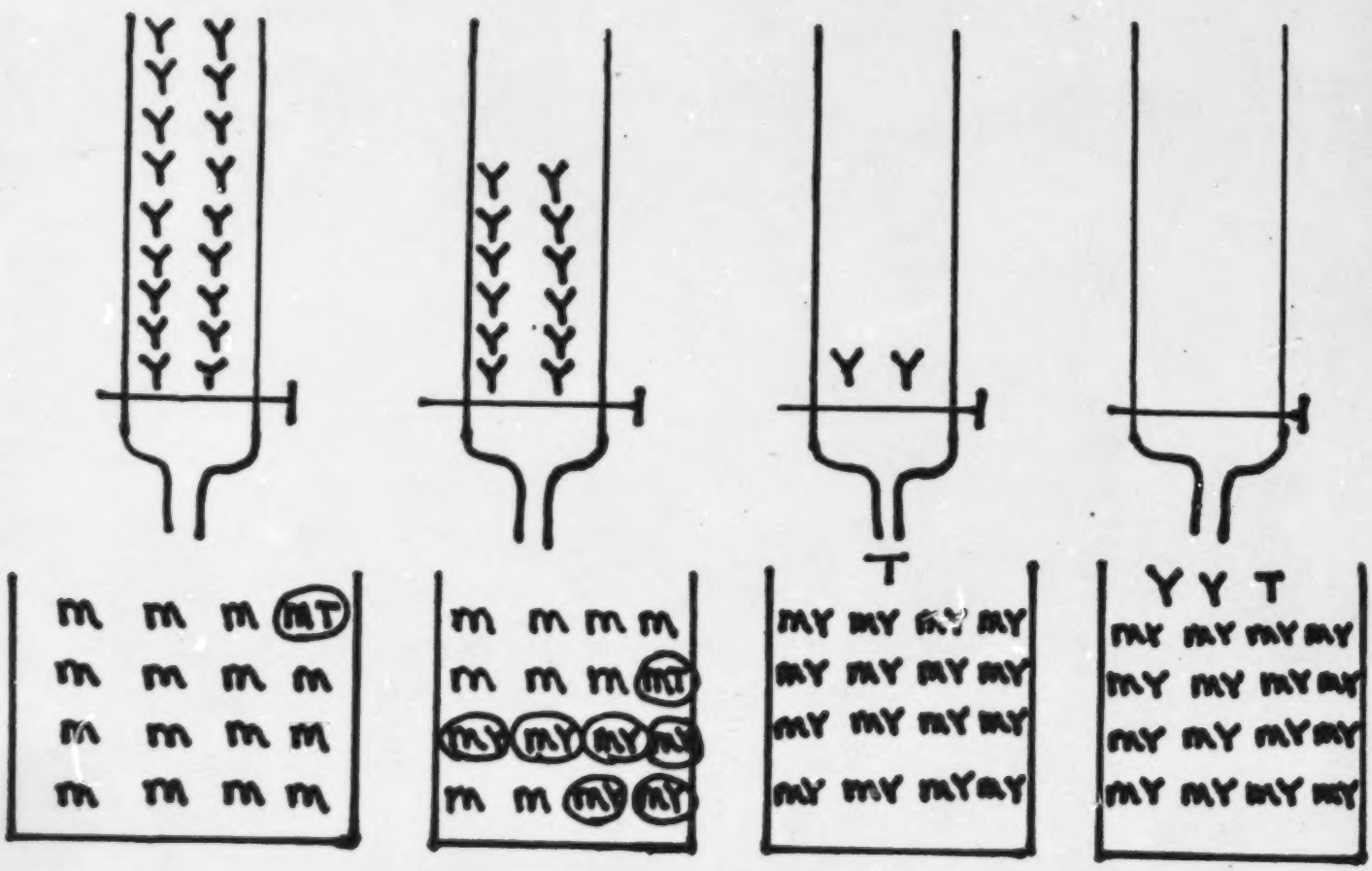
Indicator

0.5 g Eriochrome Black T, 4.5g $NH_2OH \cdot HCl$, Dilute to 100 ml. with 95% ethanol.

Transparency HD 3
Titration Diagram

Metal ion = M EDTA = Y

indicator = T



Before Titration	During Titration	At End Point	Past End Point
red	red	blue	blue

MT red T blue

TRANSPARENCY HD4

Inhibitor Chart

1. Inhibitor I CN^-
2. Inhibitor II S^{2-}
3. Inhibitor III NH_2OH

Maximum concentration allowable with inhibitors

Substance	INHIBITOR I	II	III
	mg/l	mg/l	mg/l
Al	20	20	20
Ba	*	*	*
Cd	*	20	*
Cu	30	20	0.3
Fe	30	5	20
Pb	*	20	*
Mn	*	1	1
Ni	20	0.3	0
Sr	*	*	
zn	*	200	

*titrates as hardness